[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Influence of Steric Configuration on the Ultraviolet Absorption of "Fixed" Benzils[1,2]

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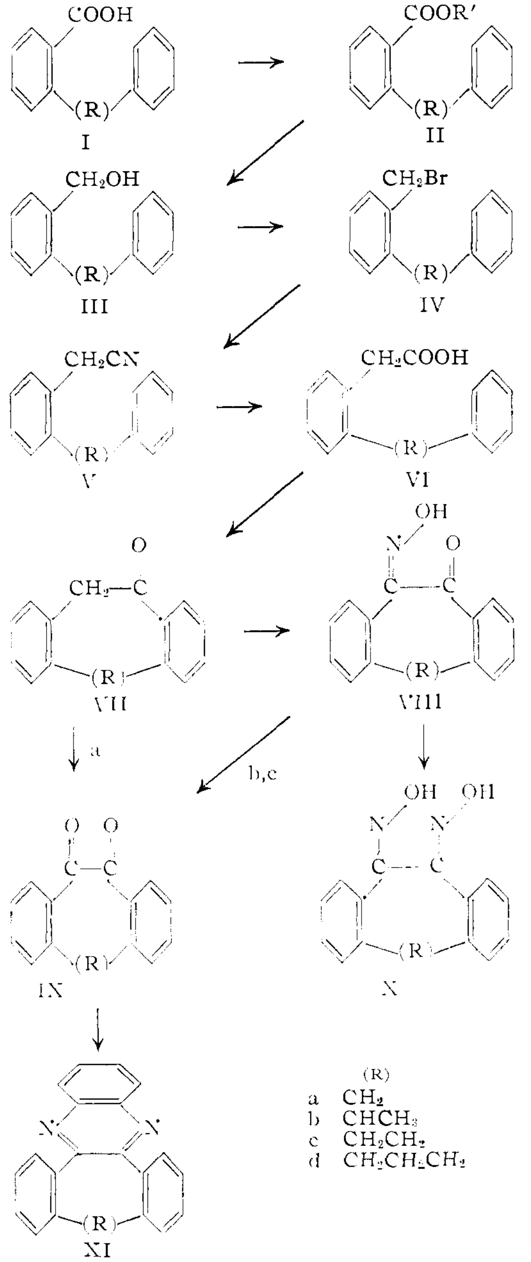
5-Methyldibenzo[*a*,*d*]cyclohepta[1,4]diene-10,11-dione (IXb) and 11,12-dihydrocycloöcta[*a*,*e*]dibenzene-5,6-dione (IXc) have been synthesized by efficient yet lengthy procedures starting with 2-(α-phenylethyl)-benzoic acid and 2-(β-phenylethyl)-benzoic acid, respectively. Structure establishment of the diketones was based upon their chemical conversions and upon the infrared absorption spectra of their intermediates. Isomers IXb and c, which can be regarded as "fixed" analogs of benzil with the geometry of the molecule determined by the size of the central ring, have ultraviolet absorption spectra markedly different from each other and from that of the open model, *o*-tolil. The position of the long wave length maximum is dependent primarily upon the magnitude of the inter-carbonyl angle in these diketones. The possibility of isomerization of IXa and IXb to substituted tropolones also has been investigated.

It has been established previously, using a series of alicyclic 1,2-diketones, that the position of the long wave length ultraviolet absorption band is dependent upon the angle between the planes of the carbonyl groups; thus, the band moves toward shorter wave length as the angle increases from 0 to 90° and shifts back again toward longer wave length as the angle increases beyond 90°.[4] It also has been shown, in a study of sterically hindered benzils, that the dicarbonyl absorption maximum is shifted to longer wave length with increasing hindrance at the *o*-carbons of benzil, corresponding to increasing tendency to coplanarity of the two carbonyl groups (probably 90 → 180°).[5] The information that was still lacking was the location of the dicarbonyl absorption maxima for compounds of the benzil type in which the two carbonyl groups approached *cis* coplanarity rather than *trans* coplanarity. We felt that this information might be provided by a study of "fixed" benzils in which the steric configuration of the carbonyl groups was somewhat restricted by linking the *o*-carbons of the two rings through an alkylene group of varying size (IX).[6]

When less conventional methods failed to produce the desired diketones IX, we resorted to a straight-forward reaction sequence, illustrated in the accompanying diagram (I → IX). 2-(γ-Phenylpropyl)-benzoic acid (Id) was obtained by treatment of *o*-phthalaldehydic acid with β-phenylethylmagnesium bromide, followed by reduction of the 3-(β-phenylethyl)-phthalide. The esters prepared from this acid and from 2-benzylbenzoic acid (Ia),[7] 2-(α-phenylethyl)-benzoic acid (Ib),[8] and 2-(β-phenylethyl)-benzoic acid (Ic)[9] were reduced with lithium aluminum hydride to the correspondingly substituted α-toluols (III). These were converted in good yields through the α-tolyl bromides (IV) and α-tolunitriles (V) to the acids: 2-benzyl-α-toluic acid (VIa), 2-(α'-phenylethyl)-α-toluic acid (VIb) and 2-(β'-phenylethyl)-α-toluic acid (VIc), but the reaction sequence conducted in the same manner failed to give VId. Ring closure of VIa, b and c was best effected by means of polyphosphoric acid, giv-



(R)
a CH$_2$
b CHCH$_3$
c CH$_2$CH$_2$
d CH$_2$CH$_2$CH$_2$

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[2] This work was supported in part by a grant from E. I. du Pont de Nemours and Co., Inc.

[3] Eli Lilly and Co. Fellow, 1952–1953.

[4] N. J. Leonard and P. M. Mader, This Journal, **72**, 5388 (1950).

[5] N. J. Leonard and E. R. Blout, *ibid.*, **72**, 484 (1950).

[6] This project was initiated by P. M. Mader; see Ph.D. Thesis, University of Illinois, 1950.

[7] E. de B. Barnett, J. W. Cook and I. G. Nixon, *J. Chem. Soc.*, 504 (1927).

[8] E. Bergmann, *J. Org. Chem.*, **4**, 1 (1939).

[9] A. C. Cope and S. W. Fenton, This Journal, **73**, 1673 (1951).

ing, in the case of VIa, dibenzo[*a,d*]-cyclohepta-[1,4]diene-10-one (VIIa),[10] previously synthesized by Rigaudy and Nedelec[11] and isomeric with the 5-ketone also possessing the linear six-seven-six fused ring system.[9,12–18] Compound VIIa and 5-methyldibenzo[*a,d*]cyclohepta[1,4]diene-10-one (VIIb) had infrared spectra which confirmed the presence of the *o*-disubstituted benzene and aryl ketone moieties. Ring closure of VIc furnished 11,12-dihydrocycloöcta[*a,e*]dibenzen-5(6H)-one (VIIc),[10,19] representative of the known six-eight-six fused ring system.[20–24]

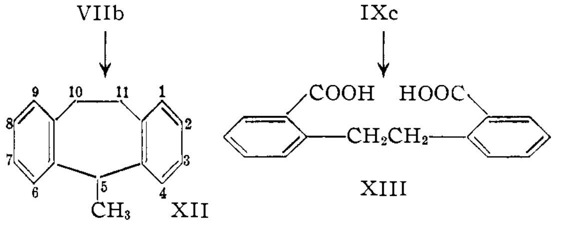
The wave lengths of the ultraviolet absorption maxima of the ketones VII, as given in Table I for solutions in 95% ethanol, are consistent with those of benzocycloalkanones having seven-[25,26] and eight-membered rings.[26,27] The intensities of the main bands are diminished in going from the seven- to the eight-membered ring tricyclic molecules (compare VIIb and c), in accord with the principle of Hedden and Brown[26] relating this phenomenon to the twisting of the carbonyl group out of the benzene plane.[27]

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF MONOKETONES

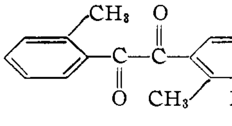
VII	λ, mμ	log ε	"Band C"[26] λ, mμ	log ε	"Band B"[26] λ, mμ	log ε
a	217	4.13	244	3.93	288	3.27
b	218	4.23	245	3.89	290	3.47
c	216	4.07	246	3.84	287	3.26

The ketones VIIa, b, c formed oximes and 2,4-dinitrophenylhydrazones, and the α-methylenic grouping present in each was indicated by the preparation, in uniformly excellent yield, of isonitrosoketones (VIIIa, b, c) on treatment with butyl nitrite and sodium ethoxide at low temperature. The isonitrosoketones were converted to dioximes (Xa, b, c) by treatment with hydroxylamine hydrochloride and pyridine, and to diketones in two cases (IXb, c) by means of formalin and hydrochloric acid. Dibenzo[*a,d*]cyclohepta[1,4]diene-10,11-dione (IXa) was obtained from VIIa by selenium dioxide oxidation in glacial acetic acid, the method used by Rigaudy and Nedelec,[11] who also established the structure of this diketone by quinoxaline formation and by benzilic acid rearrangement of the diketone to anthracene-9-carboxylic acid. The vicinal location of the two ketone groups in 5-methyldibenzo[*a,d*]cyclohepta[1,4]diene - 10,11 - dione (IXb) and 11,12-dihydrocycloöcta[*a,e*]dibenzene-5,6-dione (IXc), already indicated by their process of formation, was established further by the fact that they formed quinoxalines (XIb, c) in excellent yield. While the structures assigned to the diketones (IXb, c) were amply indicated by the interconversions within each series (b, c), final proof was achieved by relating them to known compounds. Thus, 5-methyldibenzo[*a,d*]cyclohepta-[1,4]diene-10-one (VIIb) was reduced by the Wolff–Kishner method to the known 5-methyldibenzo-[*a,d*]cyclohepta[1,4]diene (XII),[9] and 11,12-dihydrocycloöcta[*a,e*]dibenzene-5,6-dione (IXc) was oxidized by means of hydrogen peroxide in acetic acid to bibenzyl-2,2′-dicarboxylic acid (XIII), identical with an authentic sample.



XII XIII

The most striking difference between the isomers IXb and IXc lies in their color. Both seven-membered ring compounds (IXa, b) are yellow, while the eight-membered ring compound is colorless in the solid state and practically colorless in solution.[28] Their difference in absorption of light is indicated further by comparison of their ultraviolet absorption spectra in 95% ethanol solution, with *o*-tolil (XIV) as a model having equivalent *o,o*′-dialkyl substitution but with the central ring opened. The interpolated values of the absorption maxima



XIV

for dibenzo[*a,d*]cyclohepta[1,4]diene-10,11-dione (IXa), 5-methyldibenzo[*a,d*]cyclohepta[1,4]diene-10,11-dione (IXb), 11,12-dihydrocycloöcta[*a,e*]dibenzene-5,6-dione (IXc) and *o*-tolil are given in Table II. The curve for IXc bears some resemblance to those of the 3,3′-dialkoxybenzils, wherein the long wave length maximum for benzil appears as an inflection point, and to those of 2,2′- and 4,4′-dialkoxybenzils, in which the inflection point is not even discernible.[28] The long wave length absorption maximum for half-hindered benzils (mesityl phenyl diketone, mesityl *p*-tolyl diketone, mesityl 2,4-xylyl diketone, phenyl 2,4,6-triethylphenyl diketone, duryl phenyl diketone and isoduryl phenyl

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(10) *C. A.* nomenclature system.

(11) J. Rigaudy and L. Nedelec, *Compt. rend.*, **236**, 1287 (1953).

(12) E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. soc. chim. France*, 684 (1951).

(13) E. D. Bergmann, D. Ginsburg, Y. Hirshberg, M. Mayot, A. Pullman and B. Pullman, *ibid.*, 697 (1951).

(14) W. Treibs and H. J. Klinkhammer, *Chem. Ber.*, **84**, 671 (1951).

(15) G. L. Buchanan, *Chemistry & Industry*, 855 (1952).

(16) E. D. Bergmann and D. Ginsburg, *Bull. Research Council Israel*, **1**, No. 3, 120 (1951).

(17) E. D. Bergmann, J. Hoarau, A. Pacault, A. Pullman and B. Pullman, *J. chim. phys.*, **49**, 474 (1952).

(18) T. W. Campbell, R. Ginzig and H. Schmid, *Helv. Chim. Acta*, 1489 (1953).

(19) In the case of this compound, it seems fitting to recall that W. H. Perkin, Jr., (*J. Chem. Soc.*, **109**, 815 (1916)), stated (p. 832) that it would be interesting to prepare and examine the properties of VIIc, an objective which he either did not pursue or did not realize, as a perusal of his later papers reveals.

(20) S. Wawzonek, THIS JOURNAL, **62**, 745 (1940).

(21) L. F. Fieser and M. M. Pechet, *ibid.*, **68**, 2577 (1946).

(22) G. Wittig, *Angew. Chem.*, **63**, 15 (1951).

(23) G. Wittig, H. Tenhaeff, W. Schoch and G. Koenig, *Ann.*, **572**, 1 (1951).

(24) A. C. Cope and S. W. Fenton, THIS JOURNAL, **73**, 1668 (1951).

(25) C. D. Gutsche, *ibid.*, **73**, 786 (1951).

(26) G. D. Hedden and W. G. Brown, *ibid.*, **75**, 3745 (1953).

(27) W. M. Schubert, W. A. Sweeney and H. K. Latourette, *ibid.*, **76**, 5462 (1954). The authors are indebted to Dr. W. M. Schubert for providing a copy of this paper in manuscript form.

(28) Compare benzil and 4,4′-diethoxybenzil, N. J. Leonard, R. T. Rapala, H. L. Herzog and E. R. Blout, *ibid.*, **71**, 2997 (1949).

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA OF DIKETONES

Compound	λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε
IXa			249	3.71	284	3.80	425	1.75
IXb	(211	4.28)[a]	~242[b]	3.59	285	3.93	418	1.86
IXc	(211	4.51)	249	4.35	~288	3.74	~368	2.36
XIV[6,29-31]			262	4.31	~295	3.62	382	1.98

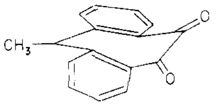
[a] Figures in parentheses may represent maxima which are not real. [b] ~ indicates an inflection point.

TABLE III

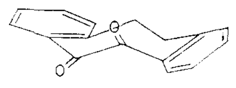
ULTRAVIOLET ABSORPTION SPECTRA OF QUINOXALINES

Compound	λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε
2-Phenylquinoxaline[37]			263	4.45	335	4.08		
2,3-Diphenylquinoxaline[37]	244	4.43	~265	4.36	345	4.07		
XIb	243	4.69	268	4.74	345	4.09	~353	4.06
XIc	241	4.48			327	4.03		
1,1,4,4-Tetramethyl-1,2,3,4-tetrahydrophenazine[4]	238	4.49			310	3.90	323	3.99

diketone) lies at 400–405 mμ, due to the average inter-carbonyl angle being changed from 90° probably toward 180°.[5] Scale molecular models indicate that conformations of 5-methyldibenzo[*a,d*]-cyclohepta[1,4]diene-10,11-dione having an inter-carbonyl angle less than 90° are the most probable (IXb′). This concept is substantiated by the long wave length maximum for IXb, which is found at 418 mμ and suggests that the inter-carbonyl angle is forced further from 90° toward 0° (*cis*-coplanarity) than it is from 90° toward 180° (*trans*-coplanarity) in the half-hindered benzils.



IXb′



IXc′

This is also consistent with the relation between angles and absorption maxima found for the alicyclic 1,2-diketones.[4] Furthermore, the diminished intensity observed for IXb in the 240–260 mμ region indicates a decreased tendency to coplanarity of the phenyl and carbonyl groups, and the general shape of the absorption curve in this region is similar to that of a fully hindered benzil such as 2,2′,4,4′,6,6′-hexaethylbenzil,[5] in which bulking at the *o*-carbons forces the phenyl and carbonyl out of coplanarity while allowing *trans*-dicarbonyl coplanarity to develop. On the basis of scale molecular models, conformations of 11,12-dihydrocycloöcta-[*a,e*]dibenzene-5,6-dione possessing a twisted or modified crown form (IXc′)[32] seem most likely, with the average inter-carbonyl angle near 90°. The absorption of IXc at shorter wave length (~368 mμ) than its isomer IXb attests to the average angle being closer to 90° in the eight-membered-ring compound. In *o*-tolil the angle is not as firmly fixed and is probably greater than 90° (compare benzil),[28] on the basis of models and the position of the long wave length maximum.

Attempts to isomerize IXa and IXb to the corresponding dibenzotropolones under conditions which had proved useful for the formation of substituted 3,7-dibenzyltropolones[33,34] were not successful. Our failure to induce the central ring of IXa[11] and IXb to become aromatic must reflect in part the resistance of this ring toward assuming coplanarity with the terminal rings and in part an unfavorable energy barrier associated with decreasing the aromatic character of the benzene rings.[15–18,35,3]

The ultraviolet spectra of the quinoxalines XIb, XIc of the diketones IXb and IXc also bear an interesting relation to each other and again reflect a difference in the geometry of the molecules (Table III, solvent 95% ethanol). The spectrum of XIc closely resembles that of a 2,3-dialkyl- or 2,3-alkylene-quinoxaline, an example of which is included in the table, indicating that the benzene rings are attached to the 2- and 3-positions in a way that permits practically no conjugation with the quinoxaline nucleus. Models show that the angles which the benzene rings make with the quinoxaline plane are about 70°, and that the eight-membered ring appears to be transformed, in this parent, to the boat form.[32] Models also suggest that in the compound containing the seven-membered ring (XIb), the benzene rings are held rather rigidly and describe an angle of 30–45° with the quinoxaline plane. Absorption for this compound occurs at longer wave length than it does for XIc and also for 2,3-diphenylquinoxaline, in which the benzene rings can be accommodated at various angles to the quinoxaline plane, with 45–60° as a reasonable average.

Experimental[38]

I. **2-Benzylbenzoic acid (Ia)**,[7] **2-(α-phenylethyl)-benzoic acid (Ib)**[8] **and 2-(β-phenylethyl)-benzoic acid (Ic)**[9] were prepared as previously described. The intermediate used for the synthesis of **2-(γ-phenylpropyl)-benzoic acid (Id)** was 3-(β-phenylethyl)-phthalide, prepared as follows. To the Grignard reagent obtained from 185 g. (1 mole) of β-phenethyl bromide and 24 g. (1 gram atom) of magnesium in 800 ml. of ether was added 64 g. (0.4 mole) of *o*-phthalaldehydic acid[39] in small portions. When the addition was complete the reaction mixture was stirred one hour at 25° and then decomposed with dilute hydrochloric acid. The ethereal solution was washed with dilute aqueous sodium carbonate, dried and evaporated. Following the removal of ethyl-

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(29) R. C. Fuson and A. I. Rachlin, THIS JOURNAL, **68**, 343 (1946).

(30) M. S. Kharasch, W. Nudenberg and S. Archer, *ibid.*, **65**, 495 (1943).

(31) The sample of *o*-tolil was kindly donated by Professor R. C. Fuson, University of Illinois.

(32) A. C. Cope, Abstracts of the 12th National Organic Chemistry Symposium of the American Chemical Society, Denver, Colorado, June, 1951, p. 77.

(33) N. J. Leonard and J. W. Berry, THIS JOURNAL, **75**, 4989 (1953).

(34) N. J. Leonard and G. C. Robinson, *ibid.*, **75**, 2143 (1953).

(35) T. Sakan and M. Nakazaki, *J. Inst. Polytech., Osaka City Univ.*, **1**, No. 2, 23 (1950); *C. A.*, **46**, 5036 (1952).

(36) M. Nakazaki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 739 (1951); *C. A.*, **46**, 11175 (1952).

(37) F. Bohlmann, *Chem. Ber.*, **84**, 860 (1951).

(38) Melting points are corrected and boiling points are uncorrected. We are indebted to Miss Helen Miklas and Mrs. James Brader for determination of the infrared spectra and to Mr. Katherine Pih, Mrs. Esther Fett, Mrs. Lucy Chang and Mr. Joseph Nemeth for the microanalyses.

(39) *Org. Syntheses*, **23**, 74 (1943).

benzene, the residue solidified and was recrystallized from ethanol–petroleum ether as colorless plates, m.p. 79–80°, yield 47.5 g. (50%). The infrared spectrum (Nujol mull unless otherwise specified) had a maximum at 1750 cm.$^{-1}$ characteristic of an α,β-unsaturated-γ-lactone,[40] and the expected maxima at 1605, 1500, 1090, 743 and 705 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.57; H, 5.93.

The reduction of 3-(β-phenylethyl)-phthalide was carried out with red phosphorus and hydriodic acid according to the directions applied to 3-benzalphthalide by Cope and Fenton.[9] The 2-(γ-phenylpropyl)-benzoic acid was purified by sublimation *in vacuo* or by recrystallization from aqueous ethanol, colorless needles, m.p. 88–89°, yield 85%. The infrared spectrum contained bands at 2650, 1692 and 1415 cm.$^{-1}$ characteristic of an aromatic acid,[41] along with those at 1607, 1505, 1094, 756 and 701 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.86; H, 6.42.

II. **Methyl 2-benzylbenzoate (IIa)**[42] **and ethyl 2-(β-phenylethyl)-benzoate (IIc)**[43] were known compounds. The ethyl esters IIb and IId were made from the corresponding acids with ethanol and hydrogen chloride: **ethyl 2-(α-phenylethyl)-benzoate** (IIb), b.p. 126–128° (1.2 mm.), $n^{26.5}_{\mathrm{D}}$ 1.5550, d^{27}_{4} 1.070; **ethyl 2-(γ-phenylpropyl)-benzoate** (IId), b.p. 135–137° (0.3 mm.), n^{30}_{D} 1.5463, d^{30}_{4} 1.051.

Anal. Calcd. for $C_{17}H_{18}O_2$ (IIb): C, 80.28; H, 7.13. Found: C, 80.23; H, 6.86. Calcd. for $C_{18}H_{20}O_2$ (IId): C, 80.56; H, 7.51. Found: C, 80.86; H, 7.79.

III. **The alcohols III**, made by lithium aluminum hydride reduction[44] of the esters II, had the following properties: **2-benzyl-α-toluol (IIIa)**, b.p. 114° (0.1 mm.), n^{20}_{D} 1.5950, yield 96%, selected infrared maxima: 3340, 1035, 750, 730, 695 cm.$^{-1}$; **2-(α′-phenylethyl)-α-toluol (IIIb)**, b.p. 128–129° (0.5 mm.), n^{31}_{D} 1.5853, d^{28}_{4} 1.080, yield 91%; **2-(β′-phenylethyl)-α-toluol (IIIc)**, m.p. 58–59°, needles from ethanol–petroleum ether, yield 95%; **2-(γ′-phenylpropyl)-α-toluol (IIId)**, b.p. 137° (0.2 mm.), n^{27}_{D} 1.5733, d^{30}_{4} 1.052, yield 99%.

Anal. Calcd. for $C_{14}H_{14}O$ (IIIa): C, 84.81; H, 7.12. Found: C, 84.72; H, 7.38. Calcd. for $C_{15}H_{16}O$ (IIIb): C, 84.87; H, 7.60. Found: C, 84.98; H, 7.75. Calcd. for $C_{15}H_{16}O$ (IIIc): C, 84.87; H, 7.60. Found: C, 84.56; H, 7.57. Calcd. for $C_{16}H_{18}O$ (IIId): C, 84.91; H, 8.02. Found: C, 84.94; H, 7.77.

IV. **2-Benzyl-α-tolyl Bromide (IVa).**—A mixture of 14.6 g. (0.074 mole) of 2-benzyl-α-toluol (IIIa) and 50 ml. of 48% aqueous hydrobromic acid was heated under reflux for 3 hours. The reaction mixture was cooled and diluted to 150 ml. with water. The oil which separated was collected by ether extraction, followed by the usual washing, drying and evaporating operations. The product was recrystallized as colorless slender needles from petroleum ether (b.p. 40–60°), m.p. 45–45.5°, yield 18.2 g. (95%); selected infrared maxima: 752, 725, 695 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{13}Br$: C, 64.38; H, 5.02; Br, 30.60. Found: C, 64.07; H, 5.17; Br, 30.44.

2-(α′-Phenylethyl)-α-tolyl bromide (IVb) was obtained similarly from IIIb in 97% yield, b.p. 112° (0.1 mm.), n^{21}_{D} 1.6069, d^{28}_{4} 1.292.

Anal. Calcd. for $C_{15}H_{15}Br$: C, 65.46; H, 5.49; Br, 29.04. Found: C, 65.76; H, 5.38; Br, 28.71.

2-(β′-Phenylethyl)-α-tolyl bromide (IVc) and 2-(γ′-phenylpropyl)-α-tolyl bromide (IVd) were not obtained pure but were used directly in the next reaction sequence (see below). All of the compounds IV gave a white precipitate on treatment with ethanolic silver nitrate.

V. **2-Phenylalkyl-α-tolunitriles.**—A solution of 0.25 mole of potassium or sodium cyanide and 0.2 mole of the bromide IV in 300 ml. of 95% ethanol was heated under reflux for 3 hours. Dilution with 500 ml. of water followed by extraction with ether and evaporation gave a light orange or brown oil, which was not purified but was used directly in the next step.

VI. **2-Phenylalkyl-α-toluic Acids.**—A mixture of 30 g. of the crude nitrile V, 30 ml. of water, 30 ml. of sulfuric acid and 45 ml. of acetic acid was heated at reflux temperature for 2 hours. The reaction mixture was poured into ice-water, and the oil which separated solidified either on scratching, long standing or the addition of a small amount of ethanol. The solid was purified by recrystallization from aqueous ethanol and by sublimation *in vacuo*: **2-benzyl-α-toluic acid (VIa)**, needles, m.p. 95–95.5° (reported[45] 93.5–94.5°), yield 85% (from bromide); **2-(α′-phenylethyl)-α-toluic acid (VIb)**, needles, m.p. 93–94°, yield 72%; **2-(β′-phenylethyl)-α-toluic acid (VIc)**, needles, m.p. 92–93°, yield 90%; infrared maxima at 2720, 2640, 1698, 1608, 1503 and 760 cm.$^{-1}$. The acids were soluble in concentrated (>10%) aqueous sodium hydroxide solution.

Anal. Calcd. for $C_{15}H_{14}O_2$ (VIa): C, 79.62; H, 6.24. Found: C, 79.71; H, 6.29. Calcd. for $C_{16}H_{16}O_2$ (VIb): C, 79.97; H, 6.71. Found: C, 80.27; H, 6.58. Calcd. for $C_{16}H_{16}O_2$ (VIc): C, 79.97; H, 6.71. Found: C, 80.16; H, 6.91.

The amide of VIa was the main product of alkaline hydrolysis of 2-benzyl-α-toluonitrile (Va), recrystallized from aqueous ethanol, m.p. 146.5–147°; selected infrared maxima: 3390, 3190, 1655, 758, 730 and 697 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.83; H, 6.83; N, 6.02.

Conversion of the crude nitrile Vd to the corresponding acid VId was not effected under the conditions described above; instead, a hydrocarbon was produced.

VII. **Ketones.**—Ring closure of the acids VI was best effected by means of polyphosphoric acid.[46] A mixture of 310 g. of phosphorus pentoxide and 190 ml. of 85% orthophosphoric acid, protected from moisture, was heated on a steam-bath for 2 hours with occasional swirling. To this mixture was added 10 g. of the acid VI, and the whole was heated for 5 hours. The mixture was poured into 1 l. of ice-water and extracted with benzene. The benzene extracts were washed with water, aqueous sodium hydroxide, and water, then dried and the benzene was removed. The residue solidified and was purified by sublimation and/or recrystallization: **dibenzo[*a*,*d*]cyclohepta[1,4]diene-10-one (VIIa)**, colorless needles from aqueous ethanol, m.p. 75–76° (reported[11] 72–73°), yield 81%; characteristic infrared maxima at 1676 (aryl ketone),[47] 1602 (aromatic) and 765 cm.$^{-1}$ (*o*-disubstituted benzene); **5-methyldibenzo[*a*,*d*]-cyclohepta[1,4]diene-10-one (VIIb)**, colorless prisms from petroleum ether, m.p. 90–91°, yield 66%; infrared maxima at 1673, 1600, 1497 and 750 cm.$^{-1}$; **11,12-dihydrocycloöcta-[*a*,*e*]-dibenzen-5(6H)-one (VIIc)**, colorless needles from petroleum ether, m.p. 93–94°, yield 76%; infrared maxima at 1680, 1600, 1500 and 748 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{12}O$ (VIIa): C, 86.51; H, 5.81. Found: C, 86.27; H, 6.05. Calcd. for $C_{16}H_{14}O$ (VIIb): C, 86.45; H, 6.35. Found: C, 86.13; H, 6.55. Calcd. for $C_{16}H_{14}O$ (VIIc): C, 86.45; H, 6.35. Found: C, 86.08; H, 6.22.

Oximes of the three ketones were made and recrystallized as colorless needles from aqueous ethanol: that from VIIa, m.p. 178.5–179.5° (reported[11] 184°); VIIb, 182–183°; VIIc, 158–159°.

Anal. **VIIa Oxime.** Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.87; H, 5.72; N, 6.23. **VIIb Oxime.** Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.25; H, 6.28; N, 5.86. **VIIc Oxime.** Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.09; H, 6.45; N, 5.69.

2,4-Dinitrophenylhydrazones of the ketones crystallized as needles from ethanol–ethyl acetate: that from VIIa, red, m.p. 231–232°; VIIb, red, m.p. 219–220°; VIIc, yellow-orange, m.p. 196–197°.

Anal. **VIIa 2,4-Dinitrophenylhydrazone.** Calcd. for

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[45] S. Murahashi, *Sci. Papers, Inst. Phys. Chem. Research* (*Tokyo*), **30**, 180 (1936); *C. A.*, **31**, 1381 (1937).

[46] *E.g.*, H. R. Snyder and F. X. Werber, This Journal, **72**, 2965 (1950).

[47] Reference 41, p. 119.

$C_{21}H_{16}N_4O_4$: C, 64.94; H, 4.15; N, 14.43. Found: C, 64.84; H, 3.94; N, 14.28. **VIIb 2,4-Dinitrophenylhydrazone.** Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.82; H, 4.66; N, 13.72. **VIIc 2,4-Dinitrophenylhydrazone.** Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.67; H, 4.54; N, 13.86.

VIII. Isonitrosoketones.—To an ice-cold solution of 0.04 mole of sodium ethoxide in 30 ml. of absolute ethanol was added 0.02 mole of ketone VII, followed by 0.04 mole of freshly prepared butyl nitrite added in small portions. The resulting mixture was kept in a refrigerator for 24–48 hours. Water was added to the reaction mixture, and this mixture was extracted with ether. Ether was expelled from the aqueous layer by passing an air stream through it. Hydrochloric acid was added in slight excess, and the oil which separated solidified on scratching. Recrystallization from ethanol furnished colorless needles: **dibenzo[*a*,*d*]cyclohepta[1,4]diene-10,11-dione monoxime (VIIIa)**, m.p. 194–195° dec., yield 95%; **5-methyldibenzo[*a*,*d*]cyclohepta[1,4]diene-10,11-dione monoxime (VIIIb)**, m.p. 232–233° dec., yield 92%; infrared maxima at *ca.* 3200, 1676 and 1600 cm.$^{-1}$; **11,12-dihydrocycloöcta[*a*,*e*]dibenzene-5,6-dione monoxime (VIIIc)**, m.p. 185–186°, yield 90%.

Anal. Calcd. for $C_{15}H_{11}NO_2$ (VIIIa): C, 75.93; H, 4.67; N, 5.90. Found: C, 75.76; H, 4.97; N, 5.93. Calcd. for $C_{16}H_{13}NO_2$ (VIIIb): C, 76.47; H, 5.22; N, 5.57. Found: C, 76.22; H, 5.08; N, 5.57. Calcd. for $C_{16}H_{13}NO_2$ (VIIIc): C, 76.47; H, 5.22; N, 5.57. Found: C, 76.86; H, 5.39; N, 5.76.

X. Dioximes.—These were made from the isonitrosoketones by treatment with hydroxylamine hydrochloride and pyridine in ethanol and recrystallized from ethanol (colorless): **dibenzo[*a*,*d*]cyclohepta[1,4]diene-10,11-dione dioxime (Xa)**, plates, m.p. 212–213° dec.; **5-methyldibenzo[*a*,*d*]cyclohepta[1,4]diene-10,11-dione dioxime (Xb)**, needles, m.p. 224° dec.; **11,12-dihydrocycloöcta[*a*,*e*]dibenzene-5,6-dione dioxime (Xc)**, needles, m.p. 220° dec.

Anal. Calcd. for $C_{15}H_{12}N_2O_2$ (Xa): C, 71.41; H, 4.80; N, 11.11. Found: C, 71.00; H, 4.52; N, 11.04. Calcd. for $C_{16}H_{14}N_2O_2$ (Xb): C, 72.16; H, 5.30; N, 10.52. Found: C, 72.14; H, 5.30; N, 10.57. Calcd. for $C_{16}H_{14}N_2O_2$ (Xc): C, 72.16; H, 5.30; N, 10.52. Found: C, 72.06; H, 5.33; N, 10.31.

IX. Diketones.—**Dibenzo[*a*,*d*]cyclohepta[1,4]diene-10,11-dione IXa** was synthesized by the method of Rigaudy and Nedelec[11] employing selenium dioxide oxidation of dibenzo[*a*,*d*]cyclohepta[1,4]diene - 10 - one (VIIa); yellow needles from petroleum ether (b.p. 90–110°), m.p. 164–165° with slight decomposition (reported[11] 165°); infrared maxima at 1672 and 1640 (vw) cm.$^{-1}$. The diketones IXb and c were obtained from the corresponding isonitroso ketones. A mixture of 15 ml. of 40% formalin, 7.5 ml. of 6 *N* hydrochloric acid,[48] and 2.0 g. of the isonitrosoketone (VIIIb or c) was heated on the steam-bath for 2 hours. To the cooled reaction mixture was added 50 ml. of water, and the water layer was decanted. The heavy viscous oil was recrystallized from aqueous ethanol: **5-methyldibenzo[*a*,*d*]cyclohepta[1,4]diene-10,11-dione (IXb)** yellow leaflets, m.p. 131–132°, yield 45%; selected infrared maxima at 1675, 1645 (vw), 1598, 758 and 720 cm.$^{-1}$; **11,12-dihydrocycloöcta[*a*,*e*]dibenzene - 5,6 - dione (IXc)**, colorless needles, m.p. 131–132°, yield 80%; infrared maxima at 1671, 1642 (vw), 1604, 760, 747 and 731 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54. Found: IXa: C, 80.83; H, 4.47. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: IXb: C, 81.41; H, 5.27. IXc: C, 81.26; H, 5.18.

XI. Quinoxalines.—A solution of 1.0 millimole of the diketone IX and 1.1 millimole of *o*-phenylenediamine in 10 ml. of absolute ethanol was heated under reflux for 3 hours. The **quinoxaline (XIb)** of IXb crystallized from ethanol as colorless needles, m.p. 205–206°, yield 92%; infrared maxima: 1607, 1562, 1542, 1493, 1483, 1345, 761 and 742 cm.$^{-1}$. The **quinoxaline (XIc)** of IXc crystallized from aqueous ethanol as colorless needles, m.p. 192–193°, yield 95%; infrared maxima: 1610, 1563, 1548, 1498, 1345, 763 and 755 cm.$^{-1}$. Neither compound contained oxygen.

Anal. Calcd. for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.09. Found: XIb: C, 85.34; H, 5.22; N, 8.92. XIc: C, 85.67; H, 5.30; N, 9.01.

Structure Proof. Wolff–Kishner Reduction of VIIb.—The hydrazone of VIIb was prepared from 3 g of VIIb and 3 g. of 85% hydrazine hydrate in 30 ml. of ethanol by heating 5 hours. A solution of the hydrazone (2.5 g.), once recrystallized from ethanol, and 8 g. of potassium hydroxide in 30 ml. of triethylene glycol was heated at 280° for 6 hours. The reaction mixture was diluted with water, extracted with ether, and the ether layer was dried. On fractionation of the residue following ether removal, 1.5 g. (64%) of a colorless oil was obtained, b.p. 100–102° (0.1 mm.), n^{25}_{D} 1.6040, d^{25}_{4} 1.0798 (reported for 5-methyldibenzo[*a*,*d*]cyclohepta[1,4]diene, b.p. 108–112° (0.09–0.13 mm.), n^{25}_{D} 1.6022, d^{25}_{4} 1.0789). The infrared spectra of this compound in carbon tetrachloride and carbon disulfide were very similar to the corresponding spectra of the Cope and Fenton[9] compound, except for very weak absorption in the 6 μ region for our compound, indicative of slight ketone contamination.

Structure Proof. Oxidation of IXc.—To a solution of 500 mg. of IXc in 7 ml. of glacial acetic acid was added 1 ml. of 30% hydrogen peroxide. After heating on a steam-bath for 10 minutes and cooling, another 1-ml. portion of hydrogen peroxide was added and the mixture was heated for 2 hours. The mixture was cooled and the solid which had separated was recrystallized from aqueous methanol as colorless needles, m.p. 230–231°. This compound did not depress the melting point of authentic bibenzyl-2,2′-dicarboxylic acid prepared by hydrolysis of the corresponding dinitrile.[49]

Attempted Isomerization of IXb to the Corresponding Methyldibenzotropolone.—A mixture of 250 mg. of IXb and 100 mg. of 10% palladium-on-charcoal catalyst in 10 ml. of triethylene glycol was heated under reflux for 3 hours.[33] The product was isolated following dilution with water and ether extraction. The residue was a brown oil which could not be purified. It failed to absorb infrared radiation in the 3 μ region but showed in chloroform solution, along with bands at 1665 and 1606, a new band at 1721 cm.$^{-1}$, indicating that the change which had taken place was not a simple isomerization. Attempted isomerization of IXa to the corresponding dibenzotropolone using palladium-on-charcoal in boiling diethylene glycol or ethylene glycol also failed.

2,2-Di-(*p*-tolyl)-propane.—The method used by Sabatier and Murat[50] for 2,2-diphenylpropane was extended to 2,2-di-(*p*-tolyl)-propane. A solution of 60 g. (0.53 mole) of 2,2-dichloropropane in 100 ml. of dry toluene was added over 2 hours to a stirred suspension of 40 g. of anhydrous ferric chloride in 900 ml. of dry toluene. The mixture was stirred at 25° for an additional 10 hours, than washed six times with dilute hydrochloric acid and four times with water. The toluene solution was dried, the solvent was removed, the residue was sublimed, and the sublimate was recrystallized from ethanol in the form of plates, m.p. 78–78.5°, yield 14.4 g. (12%), infrared maximum at 820 cm.$^{-1}$ (*p*-disubstituted benzene).

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.90; H, 8.99.

Attempts to convert 2,2-di-(*p*-tolyl)-propane to 2,5,5,8-tetramethyldibenzo[*a*,*d*]cyclohepta[1,4]diene - 10,11 - dione by means of oxalyl chloride and aluminum chloride, the method used by Liebermann[51] to prepare 2,7-dimethylphenanthraquinone from bi-*p*-tolyl, were unsuccessful.

2-[2′-(β-Phenylethyl)-phenyl]-2-propanol.—To a cooled and stirred solution of 0.30 mole equivalent of methylmagnesium iodide in ether was added a solution of 26.6 g. (0.105 mole) of ethyl 2-(β-phenylethyl)-benzoate (IIc) in two volumes of ether during 1.5 hours. The reaction mixture was stirred 10 hours longer at 25°, then decomposed by the addition of sufficient unsaturated aqueous ammonium chloride to give two clear layers. The ether solution was separated, washed with water, 10% aqueous sodium carbonate and water and dried. The residue after removal of ether was a light yellow viscous oil, crude yield 24.6 g. (98%), which

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[48] C. F. Koelsch and C. D. LeClaire, *J. Org. Chem.*, **6**, 516 (1941).

[49] R. C. Fuson, THIS JOURNAL, **48**, 830 (1926). We are grateful to Professor R. C. Fuson, University of Illinois, for donating a sample of bibenzyl-2,2′-dicarbonitrile.

[50] P. Sabatier and M. Murat, *Ann. chim. phys.*, [9] **4**, 253 (1915).

[51] C. Liebermann. *Ber.*, **44**, 1453 (1911).

showed a tendency to lose water on distillation, b.p. 104–106° (0.02 mm.), n^{21}D 1.5708; selected infrared maxima: 3530 and 1152 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.85; H, 8.77.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Rearrangement of Aliphatic Ethylene Oxides

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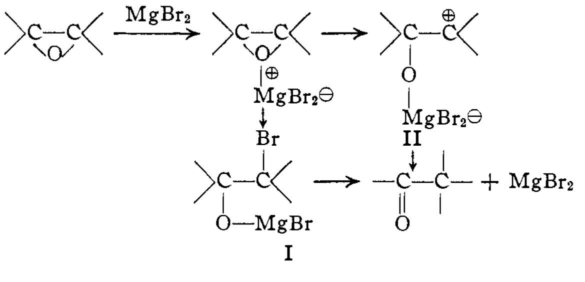
cis- and *trans*-2,3-epoxybutane have been isomerized to 2-butanone by the action of magnesium bromide. In the presence of boron trifluoride etherate the *cis*-oxide gave only 2-butanone whereas a mixture of 2-butanone and isobutyraldehyde was obtained from the *trans* isomer under the same conditions. The bromomagnesium salts of both *erythro*- and *threo*-3-bromo-2-butanol isomerized to 2-butanone. Similarly, the bromomagnesium salt of 1-bromo-2-methyl-2-propanol was converted to isobutyraldehyde, the salt of 2-bromo-3-pentanol to 3-pentanone containing 5% of the 2-isomer and the salt of 3-bromo-2-pentanol to 2-pentanone containing 20% of the 3-isomer.

The isomerization of a substituted oxirane to a carbonyl compound in the presence of magnesium bromide or a Grignard reagent may follow two different reaction paths as shown in the accompanying equations. In a study of the isomerization of the stilbene oxides,[1] the group which migrated was in part determined by the reaction conditions employed. Reaction conditions which favored rearrangement *via* a carbonium ion intermediate II (or a concerted migration of a group and cleavage of a carbon–oxygen bond of the oxirane ring) led to the formation of the same product which resulted when the related bromohydrins and glycols underwent the pinacol rearrangement. The product was the same regardless of the stereochemistry of the epoxide. However, the products obtained under conditions which favored the formation of the salt of the bromo alcohol I were dependent on the stereochemistry of the epoxide and differed from the products of analogous pinacol rearrangements in certain cases. The group which migrated when an intermediate of the type I was involved was the one predicted by the hypothesis that isomerization occurs by way of a cyclic transition state in which the oxymagnesium bromide group bonded to one carbon atom and the largest group bonded to the adjacent carbon atom are oriented *trans* to one another.[1–3] It was of interest to learn whether the above generalizations based on 1,2-diarylethylene oxide systems would be applicable to isomerizations involving 1,2-dialkylethylene oxides.[4] Since this question is of particular importance in any preparative sequence which uses such rearrangements, either independently or as the first step in the reaction of an oxirane ring with a Grignard reagent, the investigation of several aliphatic epoxides was undertaken. The results obtained with the 2,3-epoxybutanes III and IV and 1,2-epoxy-2-methylpropane (XIII) are reported here.



Both *cis*- (III) and *trans*-2,3-epoxybutane (IV)[5] have been reported[6] to yield 3-methyl-3-pentanol on treatment with ethylmagnesium bromide. The formation of this alcohol could be explained by the isomerization of each oxide to 2-butanone (V) followed by the addition of ethylmagnesium bromide. Such an explanation is consistent with our results. Treatment with magnesium bromide either in benzene or in a benzene–ether mixture converted each of the isomeric oxides III and IV to the ketone V (Table II). Similarly, both *threo*-(VI)[5] and *erythro*-3-bromo-2-butanol (VII)[5] were converted to 2-butanone (V) by treatment with one equivalent of ethylmagnesium bromide (Table I). Since magnesium bromide failed to convert the bromo alcohols VI and VII to carbonyl compounds, the rearrangement of the bromohydrins VI and VII necessarily involves either the bromomagnesium salts of the alcohols (*i.e.*, intermediates of type I) or the epoxides III and IV. Evidence bearing on this point was gained from an investigation of the 2-pentene bromohydrins VIII and IX.

Tiffeneau and Tchoubar have reported the conversion of 2,3-epoxypentane (X) to mixture of 2-pentene bromohydrins VIII and IX by the action of a cold solution of magnesium bromide.[7] 3-Bromo-2-pentanol (IX) was the predominant product in this mixture. When the oxide X was heated with magnesium bromide a mixture of pentanones XI and XII was formed in which 2-pentanone (XII) was the major product.[7] The paucity of experimental detail in this report coupled with the ab-

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[1] H. O. House, THIS JOURNAL, **77**, 3070 (1955).

[2] D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5905 (1952).

[3] F. Bergmann and A. Kalmus, *ibid.*, **76**, 4137 (1954).

[4] It seems probable that similar generalizations apply to 1,2-disubstituted ethylene oxides where one of both of the substituents are vinyl groups rather than aryl groups. The following references report cases where the treatment of such epoxides with magnesium bromide led to the migration of a vinyl group rather than a hydrogen atom. The stereochemistry of the epoxides was not stated. (a) Y. Deux, *Compt. rend.*, **207**, 920 (1938); **211**, 441 (1940). (b) M. Tiffeneau and P. K. Kuriaki, *ibid.*, **209**, 465 (1939).

[5] Only one of the enantiomorphic structures of the racemate employed has been pictured.

[6] F. H. Norton and H. B. Hass, THIS JOURNAL, **58**, 2147 (1936).

[7] M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **207**, 918 (1938). The stereochemistry of the 2,3-epoxypentane was not stated.